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Efficacy of sorption materials for nickel, iron and manganese removal from water

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Abstract

Some uncommon elements can sometimes be present in groundwater and surface water. Metals belong to such elements. Increased concentrations of iron and manganese can be expected in groundwater but higher concentrations of metals such as nickel or arsenic are not typical of such water. Nevertheless, water sources exceeding prescribed limits for drinking water in arsenic and nickel concentrations can also be found. Because of the toxicity of these metals, we started to make a research into the possibilities of removing these elements from water. Our research is funded by a grant from the Brno University of Technology.

There is a number of ways to remove heavy metals from water. Sorption on granular media based on iron oxides and hydroxides is currently the most used option. Our experiment was carried out using sorption materials GEH, CFH 0818, CFH 12 and Bayoxide, which are primarily designed to remove arsenic from water. We prepared four columns of an inner diameter of 4.4 cm for the purpose of the experiment. The thickness of the filtration media was 0.62 cm on average. Nickel, iron and manganese pollution was simulated in a laboratory. The efficacy of metals removal by four selected sorption materials was compared. During the experiment, the flow rate was set to reach the required retention time of 2.5, 7 and 15 minutes.

We have found out that the nickel concentration was reduced according to Regulation No. 252/2004 setting the limit value even after the shortest retention time (2.5 mins). Longer retention time had no significant effect on nickel removal. Our measurements also proved that all sorption materials have the ability to remove iron and manganese from water. Bayoxide sorption material achieved the best results in nickel, iron and manganese removal from water.

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1. Introduction

Groundwater and surface water sometimes contain substances that do not occur frequently in such water. Such substances include some of the metals. Increased iron and manganese content is expected in groundwater; however, metals such as nickel and arsenic in high quantities are not typical of such water. Still, there are sources where the occurrence of nickel, arsenic and other metals is in concentrations exceeding the prescribed values for drinking water.

Nickel can be found in minerals usually with sulphur, arsenic and potentially with antimony. These are, for example, gersdorfite (NiAsS), pentlandite [$(Fe,Ni)_9S_8$], nickeline (NiAs), millerite (NiS) and garnierite and pyrrhotite. It is also included in some of the aluminosilicates (serpentine). Anthropogenic sources of nickel include mainly wastewater from metal surface treatment where it is predominantly complexly bound, and wastewater from colour metallurgy. It is also used in ceramic and glass making industries and for some chemical syntheses as a catalyser. Another potential sources are nickel-plated parts of equipment that can in touch with water [1].

Besides simple Ni^{2+} ions, water in alkaline environment contains also hydroxo-complexes $[NiOH]^+$ - $[Ni(OH)_4]^{2-}$, then carbonato-complex $[NiCO_3(aq)]^o$ and sulphato-complex $[NiSO_4(aq)]^o$. Wastewater coming from galvanisation includes nickel usually in the form of cyano-complexes $[NiCN]^+$ - $[Ni(CN)_4]^{2-}$ and ammino-complexes $[NiNH_3]^{2+}$ - $[Ni(NH_3)_6]^{2+}$.

Nickel solubility in water is restricted either by carbonate $NiCO_3(s)$ or hydroxide $Ni(OH)_2(s)$. Sulphides are present, NiS(s) may also be considered.

Many studies demonstrated that some heavy metals (Ni, Cr and Cd) are complex carcinogens, and the mechanisms underlying these carcinogenesis are multifactorial. The major mechanisms of Ni carcinogenesis include aberrant gene expression, inhibition of DNA methylation, inhibition of DNA damage repair and apoptosis, and induction of oxidative stress. IARC classified metallic nickel in group 2B (possibly carcinogenic to humans) and nickel compounds in group 1 (carcinogenic to humans) [2].

Natural nickel background in groundwater is considered as concentrations that are not above ca. 20 μg/L. In sea water, the Ni concentrations reach between 0.1 - 2 μg/L. Flush water from metal surface treatment reaches nickel concentrations of tens up to hundreds of mg/L. For water intended for fish breeding it is recommended that the Ni concentration should not exceed the value of 0.1 mg/L. The same concentration is recommended for water used for irrigation purposes. The general pollution standard of permissible surface water pollution for nickel is 0.04 mg/L. Industrial wastewater discharged into municipal sewerage systems is subject to the concentration limit of 0.1 mg/L, when discharged into surface, water from electro-technical operations have a permissible nickel concentration set at 0.5 mg/L and for water discharged from metal surface treatment it is 0.8 mg/L [1].

For the quality of drinking water and the quality of table water and baby water the limit value is set at 20 μg/L. Average nickel concentrations in public drinking water systems in the Czech Republic are usually ca. 4.7 μg/L [1]. Drinking water rarely contains more than 20 μg/L of nickel, although elevated levels are possible in ground waters when contaminated by natural nickel deposits, or both surface and ground waters contaminated by industrial sources. Perinatal mortality is considered the major risk from nickel in drinking water with a WHO guideline set at 20 μg/L [3].

There are several technological methods for the removal of heavy metals and metalloids in water treatment: precipitation, ion exchange, membrane technologies, adsorption, electrochemical processes, and recently also biological methods [4].

2. Methodology

Some drinking water natural resources contain nickel concentrations that sometimes exceed several times the limit concentrations in drinking water as defined by Regulation No. 252/2004 Sb. For this reason, we focused on removing

Ni from water and during the experimental measurement we assessed the efficiency of its removal from water during filtration using various sorption materials. The measurement was carried out at the Faculty of Civil Engineering of the BUT in the laboratory of the Institute of Municipal Water Management.

For the experiment we used four filtration materials primarily designed to remove arsenic from water. These are materials CFH 0818, CFH 12, GEH and Bayoxide E33. At the same time, iron and manganese removal efficiency was examined during the filtration.

2.1. Description of sorption materials

Materials CFH 0818 and CFH 12 that are based on iron oxide hydroxide are used to remove mainly As, Se, P, Ag, Ni, Pb, Mo, Si, V, Cu and other metals from water. Sorbents have the shape of granules, whose properties are very similar and they mainly differ in terms of granularity (Table 1). They are manufactured by Lemura based in Finland. The distributor of the material in the CR is Kemwater ProChemie s.r.o. based in Bakov nad Jizerou. Photos of both types of materials you can see in the Figure 1 and Figure 2.

Table 1. Granulity of filtration materials CFH [5].

CFH 0818		CFH 12	
Dispersion [mm]	Presence [%]	Dispersion [mm]	Presence [%]
2 – 0.5	97.6	2 – 0.85	92.7
< 0.5	2.4	< 0.85	5.9
> 2	0	> 2	1.4

Fig. 1. Sorption material CFH 0818.

Fig. 2. Sorption material CFH 12.

Sorption material GEH based on granulated iron hydroxide is suitable for economical and efficient removal of arsenic and antimony from water. The material was developed by Berlin University, Department of Water Quality. It is manufactured by the German company GEH-Wasserchemie GmbH. It is imported to the CR by Inform-Consult Aqua s.r.o. Příbram. The treatment technology consists in the adsorption of the contaminant on granulated iron hydroxide (GEH sorbent) in a reactor through which the treated water flow flows. The adsorption capacity of the material depends on operating conditions [6, 7]. Photo of sorption material GEH you can see in the Figure 3.

Fig. 3. Sorption material GEH.

Bayoxide is a dry crystalline granulated sorbent based on iron oxide. It was developed by Severn Trent in cooperation with Bayer AG and produced by LANXESS Deutschland GmbH, Leverkusen in Germany. It is produced in two variants, Bayoxide E33 and Bayoxide E33P. The difference is that Bayoxide E33 is granulated whereas Bayoxide E33P is produced in the form of tablets. The material was designed to remove arsenic and its advantage is the removal of AsIII and AsV along with the removal of iron and manganese. The producer gives water treatment capacity at the arsenic content of 11 – 5 000 μg/L and iron content of 50 – 10 000 μg/L [6, 8]. Photo of sorption material Bayoxide E33 you can see in the Figure 4. The overview of sorption materials properties shows Table 2.

Fig. 4. Sorption material Bayoxide E33.

Table 2. Sorption materials properties overview. [9]

Parameter	Unit	GEH	CFH	Bayoxide E33
Chemical composition	-	$Fe(OH)_3$ + β Fe-O-OH	Fe-O-OH	Fe_2O_3 + α Fe-O-OH
Particle size	mm	0.2 - 2	1 - 2	0.5 - 2
Density	g/cm^3	1.25	1.12	0.45
Specific surface	m^2/g	250 - 300	120	120 - 200
Working pH content	-	5.5 – 6.5	6.5 – 7.5	6.0 – 8.0
Porosity of the grains	%	72 - 77	72 - 80	85
Colour	-	dark brown to black	brown to brown-red	amber
Description	-	moist granular	dry granular	dry granular

2.2. Measuring procedure

Each sorption material was poured into a glass tube with an inner diameter of 4.4 cm, with a drainage layer at the bottom made of stones, diameter of 1 - 2 cm, followed a layer of glass beads, diameter of 4 mm and then a layer of beads, diameter of 2 mm. This prevented from the escape of loose material from the column during filtration. The height of the filtration medium was 62 cm on average. The filtration columns were fixed to the wall next to each other.

The entire filtration system consisted of a vessel with raw water, pump, flow meter, set of filtration columns and vessels for the filtrate. The filtration system scheme for one column is shown in Figure 5.

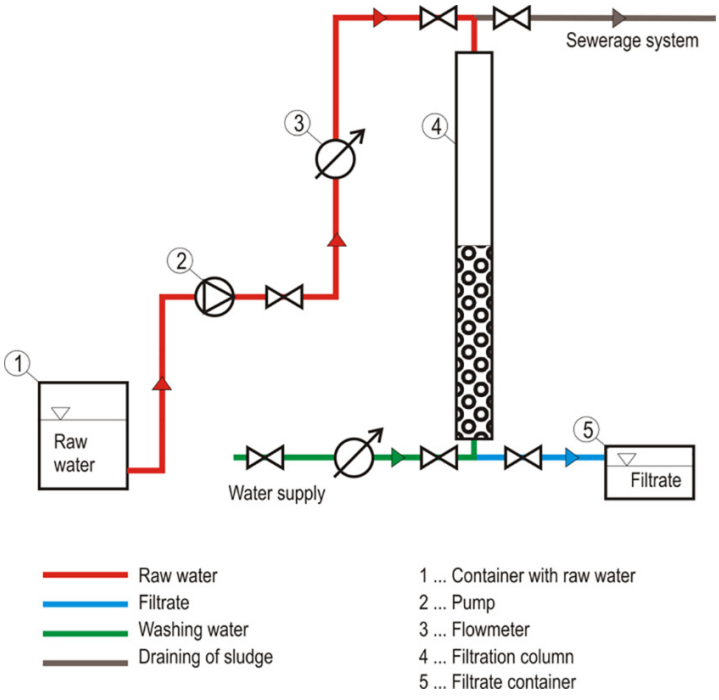

Fig. 5. Diagram of the filtration system.

Before starting the filtration, the filtration material was processed as instructed by the producer. After that, the filters were flushed with tap water, in a reverse direction from filtration, i.e. bottom up, where the flush water was discharges into sewerage. During the flushing, the flow-rate through the column was selected so as to avoid the filtration material in suspension being flushed out. The filter flushing usually lasted until clear water started flowing out of the column.

Raw water with increased concentration of nickel, iron and manganese (Table 3), this was simulated in a laboratory by adding chemical concentrates of these metals into drinking water from the Brno public water supply system. During the measurement, the raw water was pumped via a flow meter with flow rate values set in a way achieving the required retention time in the columns of 2.5 minutes, 7 and 15 minutes. Water filtered through the sorption materials had the following set concentrations of iron, manganese and nickel.

Table 3. Analysis of raw water.

t [min]	pH [-]	Turbidity [FNU]	c Fe [mg/L]	c Mn [mg/L]	c Ni [µg/L]
0	7.0	5.76	1.500	0.609	720.0

3. Results

The analyses indicate that all sorption materials achieve excellent results in nickel removal thanks to its concentrations in raw water. Even the shortest retention time (2.5 min) ensures lower nickel concentration in raw water than the highest limit value in drinking water as per Regulation No. 252/2004 Sb. If the retention time was longer, there was no major increase in the nickel concentration reduction.

For sorption material CFH 0818 occurred during a longer residence time to increase the nickel concentration, but this may be due to measurement inaccuracies. We assume here that ability of CFH 0818 is to remove nickel to final concentration of units of µg/L where the initial concentration of nickel was 720 µg/L.

The results of water analyses after filtration through individual sorption materials you can see in Table 4 to Table 7. Figure 6 shows comparison of the efficiency of sorption materials with respect to Ni removal from water.

Table 4. Analysis after filtration through the sorption material CFH 0818.

t [min]	Turbidity [FNU]	c Fe [mg/L]	c Mn [mg/L]	c Ni [µg/L]
2.5	1.43	0.111	0.052	2.0
7	0.66	0.116	0.034	2.0
15	0.41	0.021	0.037	5.0

Table 5. Analysis after filtration through the sorption material CFH 12.

t [min]	Turbidity [FNU]	c Fe [mg/L]	c Mn [mg/L]	c Ni [µg/L]
2.5	2.54	0.400	0.057	4.0
7	1.45	0.363	0.056	5.0
15	1.21	0.332	0.044	4.0

Table 6. Analysis after filtration through the sorption material GEH.

t [min]	Turbidity [FNU]	c Fe [mg/L]	c Mn [mg/L]	c Ni [µg/L]
2.5	1.63	0.153	0.155	10.0
7	0.70	0.142	0.153	9.0
15	0.67	0.133	0.150	9.0

Table 7. Analysis after filtration through the sorption material Bayoxide.

t [min]	Turbidity [FNU]	c Fe [mg/L]	c Mn [mg/L]	c Ni[µg/L]
2.5	0.97	0.122	0.055	1.0
7	0.45	0.179	0.047	1.0
15	0.49	0.086	0.038	1.0

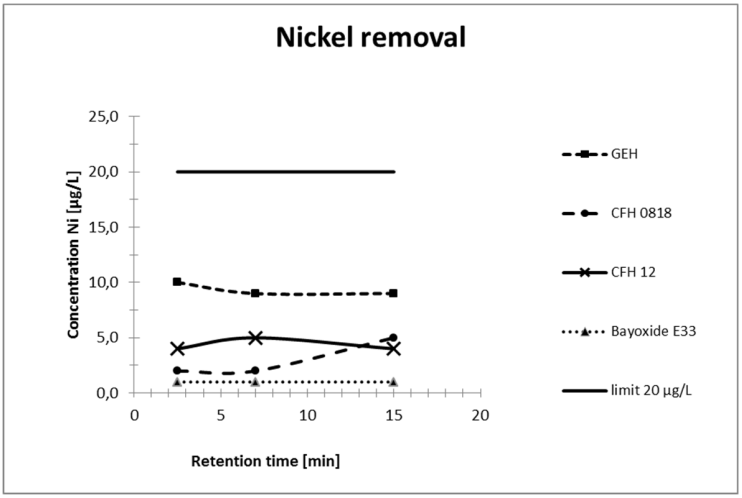

Fig. 6. Comparison of the efficiency of sorption materials with respect to Ni removal from water.

4. Conclusions

The best results of nickel removal from water was achieved by Bayoxide E33, which managed to reduce Ni content during the shortest retention time and such good results were achieved constantly throughout the measurement period. When adsorbent CFH 0818 was used, Ni concentration increased if longer retention time was used, but this might be caused by measurement inaccuracy. Given the velocity of nickel removal from water, this is contact filtration with respect to all sorption materials.

The measurement also detected that the applied filtration materials also remove iron and manganese from water. Except CFH 12, other sorbents removed iron below the limit concentration for drinking water of 0.2 mg/L. The most efficient material for iron removal seems to be sorption material CFH 0818. Manganese removal required a longer retention time than for nickel and iron to ensure the drop below the limit concentration for drinking water (0.05 mg/L). With the increasing retention time, the manganese removal efficiency increased. With the material GEH, the manganese concentration did not drop even after a contact period of 15 minutes to reach the limit prescribed value, which was probably cause by inaccurate measurement.

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